Gold recovery: Effect of ozonation on refractory gold ores prior to cyanidation

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Mineral processing of refractory gold ore is uneconomical through conventional processing methods. The ore recovery is normally below 80% due to sulphide encapsulated gold and result into high reagent consumption by carbonates. This study was conducted to investigate the use of ozone to the existing pre-treatment processes to increase the gold recoveries. To achieve this, ozone gas was bubbled in slurry at different pH values to establish the optimal pH. The resulting residue was subjected to cyanidation and Resin in Pulp (RIL) leaching to assess the effect of ozonation on gold leaching and reagent consumption. The results obtained showed that ozonation at pH 2 for 4 hours increased gold recoveries from 10% to 70%. Base metals such as arsenic, zinc and manganese were found to leach during ozonation with a recovery of 37%, 32% and 51% respectively. Ozonation improved recoveries from refractory ores with minimal cyanide and lime consumption and can prevent preg-robbing.

INTRODUCTION

The Witwatersrand gold rush brought a mineral revolution in South Africa by changing the country from an agricultural society to the largest gold producer in the world. Since the 1880's gold has continued to be one of the most sought after precious metal worldwide. Over the past years, tons of gold have been processed from the South African gold fields. Two years ago, an estimated 40, 000 tons of gold ore resources is available within the South African land and only 8000 to 10, 000 tons are economically recoverable (Crowson, 2016). The annual gold production has declined from 1000 tons in 1970 to 342 tons in 2004 and the industry has over years experienced a decline in gold price. There are continuously increasing operational costs and the depletion of free milling gold ores is on the rise (Crowson, 2016).

Cyanidation has been the standard method used to leach gold ore and recover gold since 1890 (Adams, 2016). As free milling ores are depleting, the focus has shifted to gold ores that do not yield economic recoveries after conventional cyanidation and these ores are classified as refractory ores. An ore can be refractory due to: (a) Preg robbing: gold associated with organic carbon or carbonaceous material that adsorbs leached gold during cyanidation, (b) Physical encapsulation: gold locked inside gangue material, which is difficult to liberate even after fine grinding, usually sulphides, (c) Chemical interference: gold associated with material which consumes reagents and results in the leaching process being uneconomical, (d) Leach kinetics: gold associated with minerals which cause slow leach kinetics (e.g. maldonite) (Miller, et al., 2016)

Due to the continuous depletion of free milling ores there has been a shift in focus from free milling gold ore to a more complex polymetallic and refractory ores. Processing these ores comes with additional processing routes prior to conventional cyanidation, so as to achieve economic recoveries (Davis, 2018). Additional to the processing routes, processing these ores is governed by stringent environmental regulations since they produce a by-product which has a negative impact on the environment (Davis, 2018). The pre-treatment of these ores is very crucial and depends on a thorough knowledge of the mineralogy of the ore.

Refractory ores are not oxidized; they contain either carbonaceous material or sulphide minerals. When both cases exist, the ore is said to be double refractory. Gold can also contain tellurides in rare cases; the presences of these species results in slow leaching kinetics (Ellis and Deschênes, 2016). The refractoriness of the ore can be chemical or physical (Ellis and Deschênes, 2016). Conventional grinding and cyanide leaching of refractory ores results in incomplete gold recoveries, as a solution, a pre-treatment process should be implemented. Various pre-treatment, methods includes roasting, bio- oxidation, high-pressure cyanide leaching and pressure oxidation. With the development of new ozone generators, that produce highly concentrated ozone with minimal energy consumption, ozonation has recently been given great attention and considered as an alternative pre-treatment process because it is environmental friendly, although its capital and operational costs have not been investigated in depth. González-Anaya et al., have previously used ozone as a means of improving gold recoveries from refractory gold ores subsequent to hypochlorite leaching. Other studies on pre-treating has been done by Rodríguez-Rodríguez, et al. (2018) and the results have shown that ozonation can be a suitable alternative to treat refractory gold ores.

The use of ozone as an alternative oxidant for refractory gold ores prior to cyanidation was evaluated as a solution to the challenges in gold mine industry. The evaluations were based on gold recoveries, percentage sulphides oxidised, and reagent consumption. The oxidation of refractory ores with ozone follows the same chemical mechanisms as those of pressure oxidation. The sulphides are oxidized to sulphate form and carbonaceous material (organic carbon) gets passivated to alleviate its adsorption characteristics which results in preg-robbing. Pyrite and arsenopyrite are the most common sulphide minerals found in refractory gold ores. The oxidation of these minerals yields sulfuric acid, sulphates, and elemental sulphur. The use of ozone to oxidize refractory ores increases the oxygen content of the ore, reduces reagent consumption and results in environmentally friendly products such as oxygen and water.

Ozone is a powerful oxidant and the standard oxidation potential for ozone is higher in acidic media (Li, et al., 2009).

$$O_3 + 2H^+ + 2e^- = H_2O^- + O_2 \quad E_0 = 2.07\,V \qquad [1]$$

$$O_3 + H_2O^- + 2e^- = 2OH^- + O_2 \quad E_0 = 1.24\,V \qquad [2]$$

Ozone has a limited solubility in water which depends on ozone concentration in gas phase. Henry's Law describes correlation between concentration of ozone in gas phase and that in solution, Equation 3 (Bazhko and Yahorava, 2017):

$$H_c = \frac{O_{3g}}{O_{3s}} \qquad [3]$$

The concentration of ozone in the aqueous phase increases linearly with its concentration in the gas phase and the concentration of ozone in the gas phase increases proportionally to ozone generation rate and inversely to the volumetric flow rate at the outlet of the generator. However, increase of the gas flow rate results in the increase of mass transfer coefficient and that result in increased amount of soluble ozone (Bazhko and Yahorava, 2017). A common problem associated with ozonation (especially for laboratory scale oxidation) is poor mass transfer of ozone to the aqueous phase and the loss of ozone to the overlying headspace (Bazhko and Yahorava, 2017). Ozone distribution between gas and liquid and solubility are affected by the size of the bubbles injected into the solution/slurry. Large bubbles cause poor distribution since they tend to rise to the surface rapidly and release the ozone-air mixture into the headspace (Bazhko and Yahorava, 2017). Smaller bubbles promote intimate mixing and better lateral distribution through the saturated zone (Bazhko and Yahorava, 2017). Design of sparger, namely pore size, play important role. In this study a borosilicate glass sparger with a sintered filter candle with porosity of four (10-16 µm) was used to generate small gas bubbles. Increasing the volume of carrier gas may produce larger bubbles with poorer diffusion characteristics. Very high rate of air sparge leads to

aquifer channelling or large gas bubbles and therefore results in poor mass transfer (Yannopoulos, 2012). Ozone distribution and subsequent rate of chemical oxidation may not improve with increased airflow.

Since pyrite and arsenopyrite are major refractory minerals in gold ores they dissolve in acidic condition in the presence of a suitable oxidising agent. Ozone has high oxidation potential (2.07 V) and would be able to oxidise and dissolve sulphides. The products of sulphides oxidation could be soluble ferric and sulphate ions (at acidic conditions, pH<2) or ferric hydroxide/oxide solids (pH>2). Therefore the acidic conditions are preferable. The oxidation process of pyrite and arsenopyrite follows the following reactions, Equation 4 and Equation 5:

$$2FeS_2 + 5O_3 + 2H_2O = 2Fe^{3+} + 4SO_4^{2-} + 2H^+ \quad [4]$$

$$FeAsS + 7O_3 + H_2O + H^+ = Fe^{3+} + SO_4^{2-} + H_3AsO_4 + 7O_2 \quad [5]$$

Ozone can either be contacted with the slurry directly or indirectly. Direct ozone contacting involves sparging the ozone gas in the slurry and the in-direct method involves adding the ore into ozone saturated water and direct contacting has proven to be the more effective method (Bazhko and Yahorava, 2017). Ozonation improves kinetics of gold leaching and reduces cyanide consumption due to oxidation of elemental sulphur (possible intermediate product of sulphide oxidation) which could coat gold particle and consume cyanide forming SCN^-. In this study we investigated the introduction of ozonation as an alternative, to the existing pre-treatment method for refractory ores, to increase gold recoveries.

EXPERIMENTAL

5 tons of ore was weighed and milled to 80% -75 µm passing. The sample was then blended and split into 10 kg bags. One 10 kg bag was split into 500 g samples and set aside for the ozonation test work. Characterization of the gold ore for gold, organic carbon, total carbon, elemental sulphur, sulphides, total sulphur and base metals analysis was conducted using Atomic Absorption Spectrometer (AAS), Inductively Coupled Plasma (ICP) and X-Ray Fluorescence (XRF). The intensive cyanidation leach was carried out using the standard bottle roll method with water to solid ratio of 2:1. pH was adjusted by addition of hydrated lime to between 10.5 – 11. After 1 hour, 10 kg/t of sodium cyanide was added and the slurry was bottle rolled for 24 h. The pH of the slurry was checked regularly and hydrated lime was added if necessary to maintain the pH at 10.5 – 11. After 24 h the slurry was filtered and the filter cake washed by re-pulping with water at a wet solid to water ratio of 1:1.5. The washed filter cake was dried in an oven at 60°C for 24 hours. The dried filter cake was analysed for gold and the filtrate for gold and base metals. The same process was conducted of the Resin In Leach (RIL) process and after 24 hours leaching ion exchange resin (50 mL/L) was added as the adsorbent followed by the addition of 3 kg/t of sodium cyanide. After 24 h the resin was screened out, washed and dried in an oven for 24 h. The slurry was filtered and the filter cake washed by re-pulping with water at a wet solid to water ratio of 1:1.5. The dried resin and filter cake were analysed for gold. The filtrate was analysed for gold and base metals. Different acid digestion tests were carried out using a 5 L reactor and HCl and HNO_3.

The ozonation tests were conducted with 30 % solid slurry loading. The initial slurry with the reactor mass was taken and the slurry was agitated at 400 rpm. After thoroughly mixing, the initial pH and Eh ware recorded. A 2 M sulphuric acid solution was added to get the desired pH. At the desired pH ozone was bubbled into the slurry. pH and Eh reading were taken every two minutes and samples were taken every 5, 15, 30, 45 min. At the end of the test the slurry was filtered. The cake was washed through re-pulping with deionised water at a 1.5: 1 L/S (m/m). The washed cake was dried overnight at 60^0C. The dry cake was then taken for cyanidation at 3 kg/t NaCN and RIL with 50 mL/L of resin. After cyanidation and RIL, the filtrates and solids were submitted for gold, base metal, and sulphate analysis.

RESULTS AND DISCUSSION

Elemental and mineralogical analysis

Table 1 shows the XRF analysis of head gold ore.

Table 1. XRF analysis of head gold ore

Constituent	Value(% w/w, unless otherwise stated)
Mg	2.24
Al	3.27
Si	18.35
Ca	3.39
Ti	0.15
Fe	14.7
Zn	0.11
Cr	0.052
Mn	0.36
As	0.30
Sulphide	4.17
Sulphate	4.90
Elemental S	0.13
Carbonate	11.92
Organic C	1.12
Au	3.03 (g/t)

The sample contained 4.17% sulphides and 1.12% organic carbon. Sulphides and organic carbon are the main causes of gold ore refractoriness (Hammerschmidt et al. 2016). At their respective compositions, preg robbing and low recoveries after conventional cyanidation were anticipated. The head gold grade was 3.03 g/t and the ore contained 11.92% carbonates. Carbonates react readily with sulphuric acid to form respective sulphates, for example, gypsum and magnesium sulphate. It was anticipated that the 2 M sulphuric acid used to control pH was going to be consumed by these carbonates. Silica was at 18.35%, it is known to seldom dissolve in acidic media during bio-oxidation and can coat dissolved gold complexes (Ellis and Deschênes, 2016). Since silicate minerals do not easily dissolve in acidic media, the gold associated with silica will not be liberated during diagnostic leaching and they could possibly coat exposed gold surfaces, affecting recoveries.

Table 2. Gold bearing mineral association

Mineral	Gold (11.8 % mass)	Electrum (88.2 % mass)
Free milling	54.2	0.4
Pyrite	15.8	91.1
Pyrrhotite	not detected	5.2
Arsenopyrite	not detected	0.5
Sphalerite	4.9	not detected
Quartz	6.4	not detected
Feldspar	16.3	0.6
Chlorite	not detected	2.1
Ankerite	not detected	0.1
Carbon	2.5	not detected
Total	100.0	100.0

Table 2 depicts the mineralogy of gold ore. A total of 88.2% gold was in the electrum form (AuAg) and the other 11.8% was gold on its own. High association levels of gold with pyrite (91.1%) in the ore indicated that the ore is refractory and low recoveries would be experienced after conventional cyanidation of the ore. Some of the gold was associated with carbon, collectively as organic and carbonates. Association with 2.5% carbon was observed and the ore was characterised as preg-robbing and high acid consuming. The presence of silica minerals (quartz and feldspar), suggested that a

significant portion of the gold would not be available for leaching during the diagnostic leach test work. This is due to silica minerals being inert under acidic conditions (Santoro et al., 2014).

Diagnostic Leach

Based on the mineral association, it was found that direct cyanidation could only recover about 9.27% of gold. From the diagnostic results, it is clear that the 9.27% recovery is mainly from free milling gold. Free milling gold is gold that is not associated with any mineral and can all be recovered by conventional cyanidation (Hammerschmidt et al. 2016). The results were therefore in line with what Wills (2015) has reported, thus, conventional cyanidation of refractory ores will only recover free milling gold. Resins were added into a conventional direct cyanidation leach and this increased gold recovery to 23%. Resin and organic carbon remove dissolved gold from solution by the same adsorption mechanism. The resin had a higher gold affinity compared to organic carbon present in the ore. This makes it more competitive in adsorption of gold and overcomes the preg-robbing of organic carbon. An increase in gold recovery from 9.27% through conventional direct cyanidation to 23% through RIL direct cyanidation indicates that the ore is actually preg-robbing, which was expected, based on the presence of organic carbon as shown in the chemical composition of the ore.

Effect of resin addition on gold recoveries

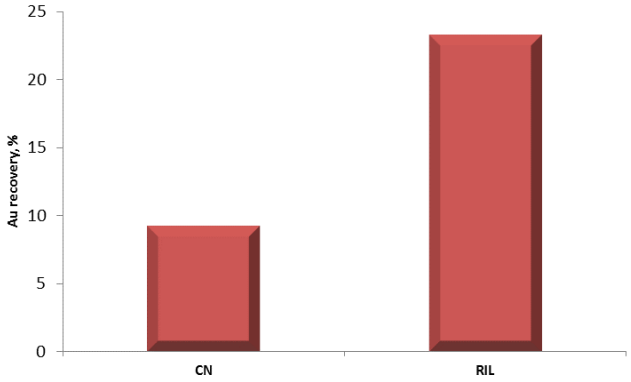

Figure 1. Effect of resin on gold recovery.

Figure 1 shows the effect of resin addition on gold recovery. The results show that RIL process significantly improved gold recoveries. About 75% of the gold was expected to be recovered after conventional RIL, acid+ RIL and roasting steps. The other 35% is associated with silica gangue and was not expected to be liberated through diagnostic leaching as silica minerals do not readily oxidise under acidic conditions.

Gold association with different mineral phases

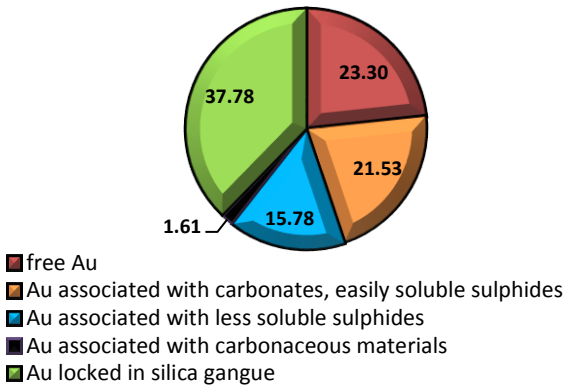

Figure 2. Gold Association with different mineral phases.

The gold association with different minerals is presented in Figure 2. From the results obtained 22% of gold was locked in carbonates and easily soluble sulphides. After these gangue minerals were dissolved in 2.5 M HCl (Hydrochloric acid), all the gold associated with these minerals was liberated.

Effect of acid leaching

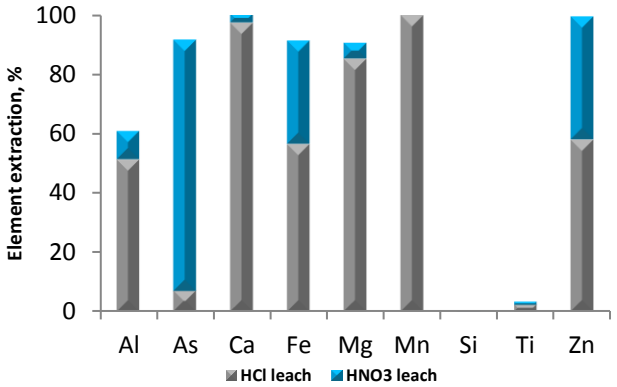

Figure 3. Solubility of various elements during acid leaching with HCl and HNO_3.

Figure 3 represents the solubility of various elements in acid leaching with HCl and HNO_3. 16% Au was recovered after leaching the sample with 27.5 % HNO_3. Analysis of HNO_3 leach liquor indicated dissolution of Fe, As and Zn minerals. Roasting of the sample aimed to destroy organic carbon and liberate gold associated with it and the gold liberation fraction was 1.6%. A total of 38% of gold could not be leached due to its association with silicates as silicates do no oxidize during acid digestion and roasting.

Ozone pre-treatment

For the ozonation tests (8 tests), as presented in Table 3 were conducted. In test 1 to 6, the slurry was pre-oxidised with ozone and the pH was adjusted. Test 7 was done without ozone with adjustment in pH. Test 8 was run with no ozone and pH adjustment.

Table 3. Acid consumption during ozonation

Test	pH	Duration, hr	Temperature, ^oC	H_2SO_4, kg/t
1	1	1	ambient	238
2	2	1	ambient	140
3	6	1	ambient	4.4
4	2	3	ambient	160
5	2	4	45	212
6	3	1	ambient	27
7	2 (no ozone)	1	ambient	218
8	Natural (8)	1	ambient	0
Theoretical consumption based on				195.5

carbonate content				

The oxidation of pyrite formed sulphate ions which reacted with hydroxide ions to form sulphuric acid and continuous addition of 2M sulphuric acid was necessary to maintain the desired pH for test 1 to test 7. The sample contained 11.92% carbonates which consumed the sulphuric acid generated during sulphide oxidation and 2 M sulphuric acid was added for pH control. Acid consumption was the highest for the test conducted at pH 1. It was noticed that acid consumption was higher when no ozone was added (test 2 compared to test 6). This proved that there was sulphuric acid generation during pre-oxidation of the sulphides with ozone. The increase of temperature also resulted in higher acid consumption (test 5 compared to test 2).

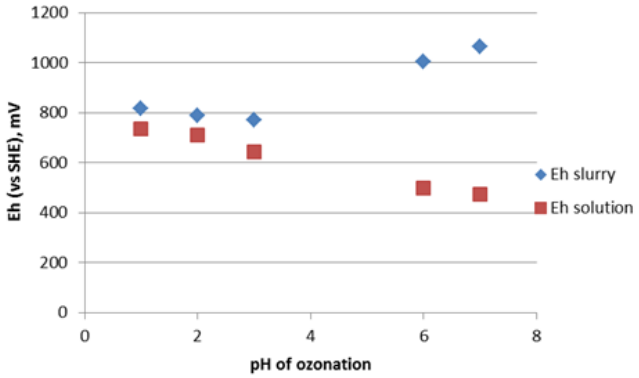

Figure 4. Eh values for ozonation tests.

The Eh values for the ozonation tests are presented in Figure 4. Five tests (tests 1, 2, 6, 7 and 8) were conducted for 1 hour at different pH. Eh of the slurry increased after 20-30 minutes in every test and thereafter remained constant. When the samples were treated at low pH (1-3), Eh of the slurry reached about 820 Mv (vs SHE) after 1 hour of treatment. For tests done at higher pH (6-8), the final Eh of the slurry was 1020 Mv (vs SHE). It was noticed that Eh of corresponding filtrates was lower compared to slurry Eh values. This difference was due to the effect of dissolved ozone on Eh value for slurries. Eh of the filtrates was measured after ozonation stopped and dissolved ozone decomposed to the surrounding air as oxygen. The Eh of the slurries after 1 hour into oxidation was lower than expected. Ozone is a very strong oxidant with an oxidizing potential of 2000 mV (Rodríguez-Rodríguez et al., 2018). Previous studies conducted by Gonzalez-Anaya et al (2011) shows that, it is possible to reach a final Eh of 1242 mV. It was expected that the Eh of the slurry be close to the oxidation potential of ozone (2000mV) or at least above a 1000 mV, but that was found to not be the case. Extended oxidation time and increased temperature were suggested (tests 3 and 4) to see if the slurry Eh could not go higher than 820 mV, to at least 1000 mV. It required 3 hours to achieve Eh 1032 mV (vs SHE) at pH 2 (test 3). Ozonation at pH 2 and 45°C conducted for 4 hours resulted in final Eh of 870 mV (vs SHE). Gases generally dissolve better at low temperatures. This is the reason why increasing temperature did not significantly increase the Eh. However, it is important to note that there was a 50 mV increase in Eh after increasing temperature. The temperature catalysed gangue consumption process, allowing ozone to only react with the gold associated sulphides and carbonates.

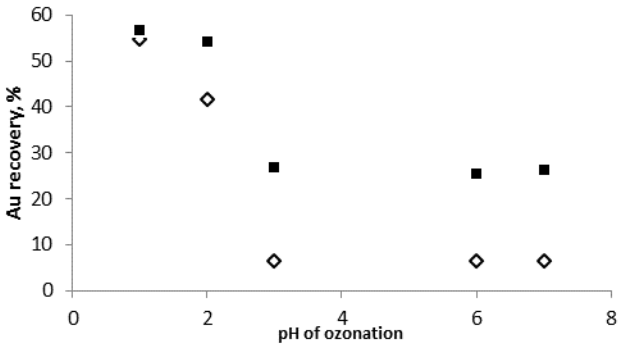

Figure 5. Effect of oxidation pH on recovery of gold

Pre-oxidised samples were subjected to cyanidation and RIL tests. Figure 5 shows that pre-oxidation with ozone improved gold recovery when treatment was done at pH 1 and 2. At pH 1 and 2, ozone dissolution is high and therefore more gold is liberated and made available for leaching. Moreover, at pH 1 cyanidation and RIL provided the same gold recovery. This indicated that ozone at ideal conditions for dissolution (low pH), can result in the oxidation of the preg-robbing organic carbon, and preg-robbing can be overcome.

Effect of pre-treatment on gold recovery

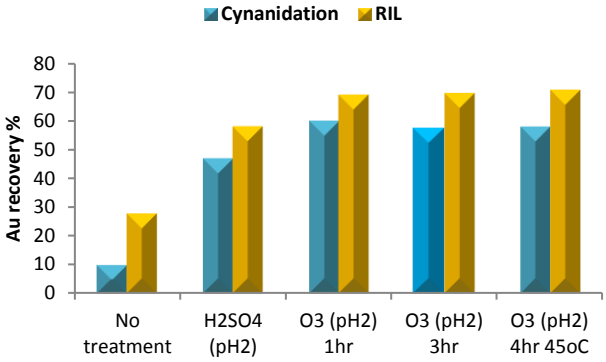

Figure 6. Effect of pre-treatment on gold recovery.

To evaluate the effect of acidification on gold recovery, test 3 was conducted at pH 2 without ozone. Figure 6 shows that treatment with acid for 1 hour increased Au recovery by 17% for both cyanidation and RIL (when compared to an untreated sample). When ozone was bubbled through the slurry for 1 hour it increased Au recovery by 34% and 26% for cyanidation and RIL, respectively. Prolonged ozonation improved Au extraction further. The difference between cyanidation and RIL was less when ozone was used to pre-treat the ore than when no ozone was used. This proved that ozone oxidised preg-robbing organic carbon in the ore.

CONCLUSIONS

From the chemical analysis, mineralogical analysis and diagnostic leaching tests, it was clear that the ore is double refractory and contains a significant composition of silica minerals (18.35%) that could interfere with gold recoveries. 35% of gold in the ore was not available for leaching after acid and roasting oxidation due to association with silica minerals. Majority of the remaining 65% gold was associated with sulphide minerals and it was necessary to pre-treat the sulphide minerals before leaching the gold because conventional cyanide leaching gave very low recoveries. The presence of organic carbon in the ore made the ore to be preg-robbing but the use of ozone to oxidize the ore was

efficient in overcoming preg-robbing of the ore. Gold recoveries increased when ozonation pre-treatment was applied compared to when there was no pre-oxidation, this proved that ozonation does possibly oxidize sulphide minerals and liberate the associated gold. There was a decrease in pH when ozonation was done without sulphuric acid addition. The decrease was due to the formation of sulphuric acid, formed as the sulphide minerals were oxidized. The cyanide consumption was almost the same for tests with pre-treatment and without pre-treatment.

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